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## Effects of land use on the spatial distribution of trace metals and volatile organic compounds in urban groundwater, Seoul, Korea

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**Abstract** To investigate the urban groundwater contamination by eight trace metals and 69 volatile organic compounds (VOCs) in relation to land use in Seoul, a total of 57 groundwater samples collected from wells were examined using a non-parametric statistical analysis. Land use was classified into five categories: less-developed, residential, agricultural, traffic, and industrial. A comparison of analyzed data with US EPA and Korean standards for drinking water showed that some metals and VOCs exceeded the standards in a few localities, such as Fe ( $N=5$ ), Mn ( $N=6$ ), Cu ( $N=1$ ), TCE ( $N=6$ ), PCE ( $N=8$ ), 1,2-DCA ( $N=1$ ), and 1,2-dichloropropane ( $N=1$ ). Among the 69 investigated VOCs, 19 compounds such as some gasoline-related compounds (e.g., toluene) and chlorinated compounds (e.g., chloroform, PCE, TCE) were detected in groundwater. Non-parametric statistical analysis showed that the concentrations of most trace metals (Fe, Mn, As, Cr, Pb, Cd) and some VOCs (especially, TCE, PCE, chloroform; toluene, carbon tetrachloride, bromodichloromethane,

CFC113) are significantly higher in the industrial, residential, and traffic areas ( $P < 0.05$ ), indicating that anthropogenic contamination of urban groundwater by those chemicals is growing. Those chemicals can be used as effective indicators of anthropogenic contamination of groundwater in urban areas and therefore a special attention is warranted for a safe water supply in those areas. The results of this study suggest that urban groundwater quality in urban areas is closely related with land use.

**Keywords** Urban groundwater · Seoul · Trace metals · Volatile organic compounds · Non-parametric statistical analysis · Land use

### Introduction

In an urban area such as Seoul, there are many potential sources leading to groundwater contamination, such as

domestic effluents, septic tanks, leaky sewage systems, gasoline stations, leachate from waste disposal sites, and spillage from industrial sites (Barber et al. 1996; Subbarao et al. 1996; Eiswirth and Hotzl 1997; Sharp 1997;

Trauth and Xanthopoulos 1997; Niemczynowicz 1999; Lerner 2002). The groundwater quality in urban area primarily depends on land use. Groundwater quality in developed urban settings, compared to those in less-developed settings, are characterized by increased concentrations of major and/or minor elements and the changes in oxidation–reduction condition (Cain et al. 1989; Anderson 1993; Eckhardt and Stackelberg 1995; Squillace and Price 1996; Barrett et al. 1999; Trojan et al. 2003; Choi et al. 2005).

A myriad of groundwater pollution sources exist in Seoul and are considered to be closely related to land use (Lee PK et al. 2001; Lee et al. 2003; Kim 2004; Choi et al. 2005). Thus, a good understanding of the control of groundwater contamination through land use will be most important and effective for the sustainable management of groundwater in Seoul. Choi et al. (2005) examined the distribution of major cations and anions in Seoul groundwater in relation to land use and found that total dissolved solids (TDS) can be used as an effective parameter for evaluating anthropogenic contamination. Little is known, however, about the relationships among groundwater quality, anthropogenic contamination sources, and land use in Seoul. Furthermore, contamination of Seoul groundwater by either volatile organic compounds (VOCs) or trace metals has not been investigated in relation to land use. The present work was initiated to elucidate the impacts of land use on groundwater contamination by trace metals and VOCs. However, these types of studies have many difficulties and limitations in ensuring whether a sample represents the intended land use and in working with statistically non-normally distributed data for concentrations of trace metals and VOCs, mainly due to their low detection frequency (Barringer et al. 1990; Eckhardt and Stackelberg 1995; Hudak and Blanchard 1997; Trojan et al. 2003). Non-parametric statistical analysis was used in this study to test the hypothesis

that the concentrations of trace metals and VOCs are significantly affected by land use. The results of this study can be effectively used to set up a guide and policy for sustainable management and protection of groundwater in urban areas in Seoul.

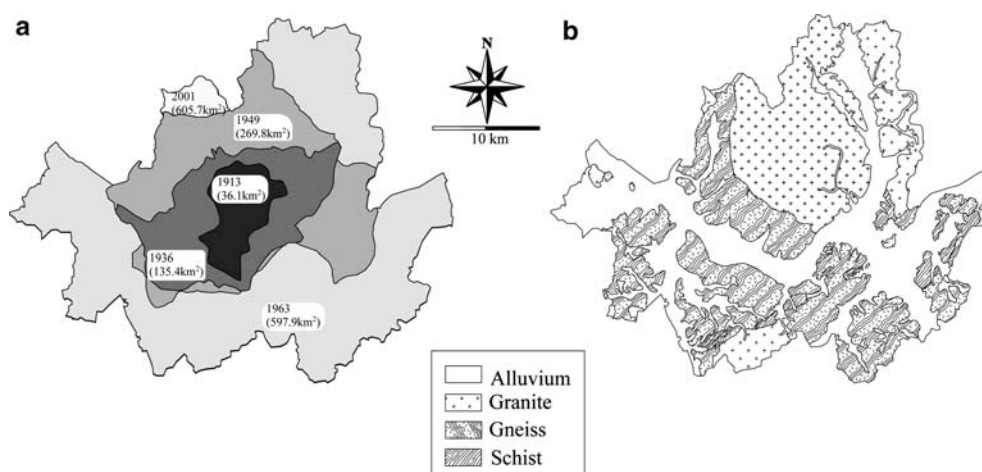
## Study area

### Physical setting and groundwater use

Seoul Metropolitan City (the capital of South Korea) is located in the mid-west of the Korean Peninsula. Seoul currently covers an area of 605.7 km<sup>2</sup>. It measures 37 km in an East–West direction and 30 km in a North–South direction. It has undergone significant and steady expansion since 1913 (36 km<sup>2</sup>), as shown in Fig. 1a. Concurrently, the population increased enormously from 1.5 million in 1949 to circa 10 million in 2001. The current population density amounts to about 17,000 people/km<sup>2</sup> (SMC 2001a). As a result of the rapid urbanization and population increase, land-use characteristics in Seoul has significantly changed: for example, large expansion of urban centers, progressive retreat of agricultural fields, increase in the number of high traffic roads, etc. Water demand has also significantly increased.

A monsoonal climate with an average annual temperature and precipitation of 11.8°C and 1,300 mm, respectively, is characteristic of Seoul (KMA 2002). About 70% of total annual precipitation falls typically as downpours in the summer months between June and September. The surface geology of the Seoul area consists of thin (<20 m) soils and alluviums and underlying crystalline rocks comprising granite and gneiss with minor schist (Chae et al. 2004; Fig. 1b). The gneiss of Precambrian age consists mainly of banded biotite

**Fig. 1** Maps showing the enlargement of Seoul City from 1913 to 2001 (a) and geologic setting (b)



gneiss and migmatitic gneiss. Granites of Jurassic age are the most widespread and characteristically crop out at high mountains surrounding Seoul. Alluvium occurs along the Han River and its tributaries and mainly comprises sand and silt with high permeability.

The municipal water supply in Seoul largely depends on surface water (especially, the Han River). The daily average of public water supply amounts to about 4 million m<sup>3</sup>/day, corresponding to a water supply per person of about 400 l/day. Groundwater occupies circa 10% of the water supply. About 15,000 wells were reported to be in use in 1999, yielding urban groundwater for domestic (75.7%), agricultural (14.5%), industrial (3.9%), and drinking (5.9%) purposes. The use of groundwater for drinking is continuously and rapidly increasing. The current annual yield of groundwater in Seoul is considered to amount to 23% of the estimated sustainable yield (SDI and SMC 2001; Lee et al. 2003). However, in addition to progressively increasing anthropogenic contamination, the local increase in groundwater pumping is considered as a major cause of progressive deterioration of the groundwater quantity and quality. Owing to the thin nature of soil and alluvium, groundwater in Seoul has largely been developed from fractured aquifers in crystalline rocks.

## Land use

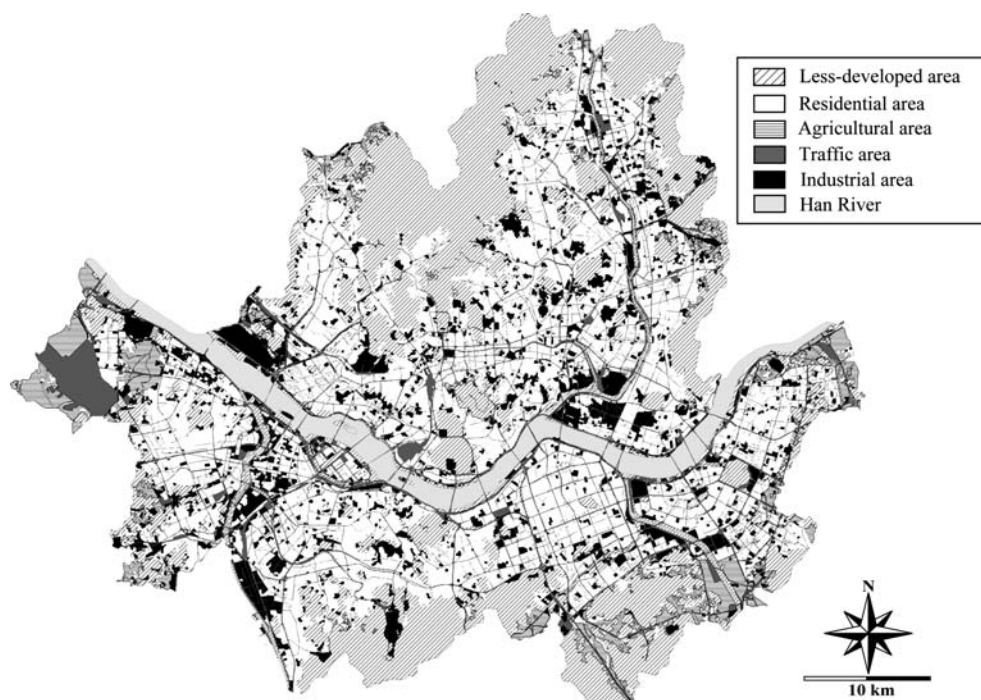
For this study, the land use in Seoul City was classified into five categories: less-developed, residential, agricultural, traffic, and industrial (Yun et al. 2000; SMC 2001b; Lee et al. 2003). The results of land-use classification are shown in Table 1 and Fig. 2. The 'less-developed' areas occupy about 37% of the total area. This includes

grasslands, forests (including Green Belts), legally inaccessible areas, rivers, streams, and wetlands. Most of the mountain forests are in the northern and southern parts of Seoul (Fig. 2). The 'residential' areas (about 37%) encompass detached houses, apartment houses, and traditional homes, and they also include the commercial and business areas, and mixed residential and business areas. The 'agricultural' areas (about 5%) are preferentially located near the western, eastern, southeastern city boundaries, where suburban agricultural activities for cropping of rice and flowers is still performed on open fields and in green houses. The 'traffic' areas occupy about 10% of the total area and include railroads, roads (dominantly, paved), airport and related facilities. More than 2 million vehicles are recently running on the roads, with an annual oil consumption of more than 80 million barrels/day (SMC 2001). Locally there is a very high traffic density (more than 12,000 vehicles/day) in the central downtown area and in main trunk roads, forming a potential source of groundwater pollution in Seoul (Choi et al. 2005). The 'industrial' areas occupy about 10% of the total area and are ubiquitous in Seoul (Table 1; Fig. 2). In such areas complex and varied factories and facilities have been located since 1970s, including small-scale light industries (e.g., textile industry, manufacture of plastic material, printing), machinery and non-ferrous metal processing industries, high-tech electronics, and urban infrastructure facilities (e.g., sewage treatment facilities, waste landfill areas, power plants, waste incineration facilities). Particularly in the southwestern part of Seoul, more than 1,000 factories are currently being operated within each administrative district. The industrial activity in Seoul has been considered as an important cause of groundwater contamination (Lee PK et al. 2001; Choi et al. 2005).

**Table 1** Land use characteristics of Seoul Metropolitan City, Korea (after SMC 2001b)

Land use	Sub-classification	Area	
		km <sup>2</sup>	%
Less-developed	Grasslands	17.5	2.88
	Forest areas	156.9	25.84
	Managed green areas	2.0	0.33
	Inaccessible areas (non-surveyable areas, military areas)	12.7	2.09
	River, streams, and wetlands	35.6	5.86
Residential	Detached houses, apartment houses, traditional houses	163.5	26.93
	Mixed residential and business area	29.8	4.91
	Commercial and business area	35.6	5.86
Agricultural	Field crop areas	29.8	4.91
Traffic	Railroad, road, airport, and related facilities	62.2	10.24
Industrial	Numerous small-scale light industries (textile industry, manufacture of plastic material, printery), machine, non-ferrous metal processing industry, high-tech electronics	8.2	1.35
	Urban infrastructure facilities (sewage treatment facilities, waste landfill areas, power plants, waste incineration facilities)	7.9	1.30
	Public facilities	30.6	5.04
	Denuded area	14.9	2.45

**Fig. 2** Land use map of Seoul, Korea (modified after SMC 2001b)



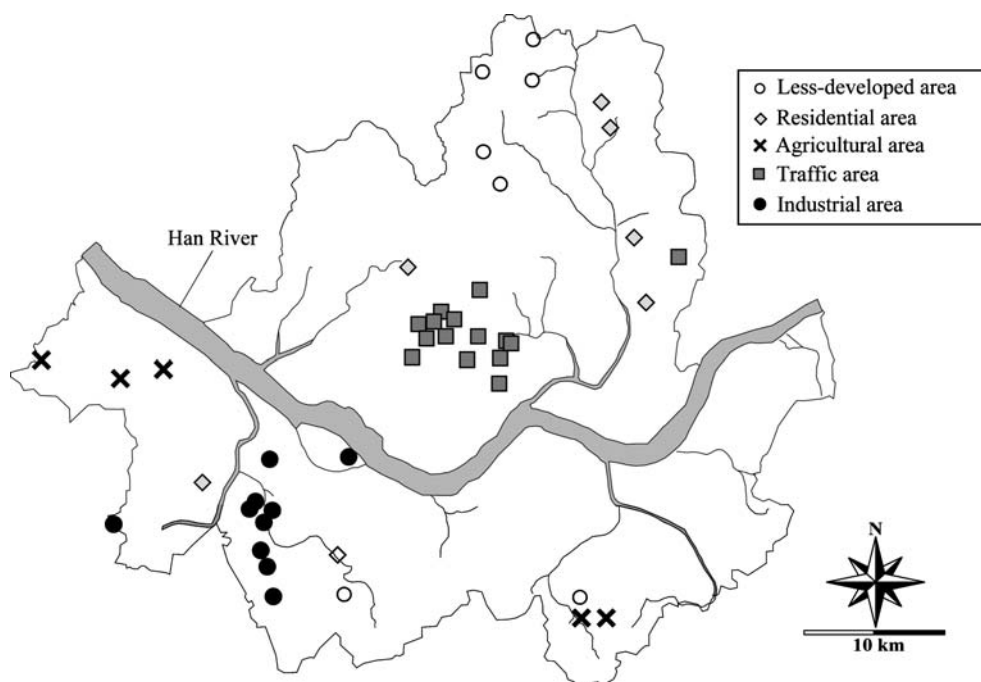
## Materials and methods

### Sampling and chemical analysis

Groundwater samples for the present study were collected during 2000 to 2001 from 57 pre-existing wells

currently in use. The localities of sampling sites were chosen on the basis of land use characteristics on both regional and local scales (Fig. 3). The average depth of chosen wells was 94 m below the land surface, thus indicating an environment of deep-fractured aquifers. All the sampling and analytical procedures followed the standard method described by APHA et al. (1992). Water

**Fig. 3** Localities of urban groundwater sampling in Seoul, Korea



samples were collected using suction pumps after purging at least three to four well volumes. Table 2 summarizes the instrumental methods used for the determining trace metals and VOCs and their detection limits.

Samples for trace metal analysis were immediately filtered through 0.45  $\mu\text{m}$  cellulose membranes and were acidified to  $\text{pH} < 2$  by adding several drops of ultra-pure nitric acid. They were kept at 4°C before the chemical analysis using ICP-MS (Perkin-Elmer SCIEX ELAN 6000). The standard solutions used for trace metal analysis were the NIST SRM 1643d standard (Trace Elements in Water) and Perkin Elmer Pure Atomic Spectroscopy standards. The percentage relative standard deviation (RSD) values determined from repeated analyses of standards and duplicate or triplicate samples were less than 5%.

Groundwater samples for the determination of VOCs were separately collected in 40 ml glass bottles with a tight Teflon cap. Special care was taken in order to minimize the evaporation of VOCs during sampling and storage. The samples were kept at 4°C under acidic ( $\text{pH} < 2$ ) conditions by adding HCl. Sixty-nine compounds belonging to VOCs were analyzed at the Korea Institute of Science and Technology (KIST) using a Gas Chromatographer (model HP5890) directly interfaced with a HP5970 mass selective detector (MSD) (Lee KJ et al. 2001). Before the GC-MSD analysis, extraction and pre-concentration of water samples were performed with a Tekmar LSC 3000 sample concentrator and an ALS 2016 purge-and-trap. The purge-and-trap was connected with GC by inserting a capillary (about 20 cm long) between the GC injection port and the purge-and-trap module. The conditions used for the purge-and-trap were: purge flow = 40 ml/min (35°C, 99.9999% He), dry purge flow = 20 ml/min (99.9999% He), sample, desorption time = 1 min, cold trap

temperature = -150°C. All chromatograms were obtained in the selective ion monitoring (SIM) mode. The conditions of the GC/MSD were as follows: ultra-2 column (cross-linked 5% phenylmethylsilicon, 50 m $\times$ 0.2 mm I.D. $\times$ 0.33  $\mu\text{m}$  film thickness); the He carrier gas set at 0.48 ml/min; 1/100 split ratio; injection port temperature = 200°C; transfer line temperature = 250°C. The standard solution used for VOCs determination was the Supel Co Stock Standard that was diluted with pure methanol solution. The analyses of field and laboratory duplicates showed the RSD values of <10%.

### Statistical analysis

Non-parametric statistical analysis (Helsel and Hirsch 1992; Hudak and Blanchard 1997; Trojan et al. 2003) was performed to verify if significant statistical differences were present among land-use categories in terms of the concentrations of trace metals and VOCs. The Kruskal-Wallis test in the software package SPSS 10.0 was used because only five land-use groups with relatively small numbers of samples (7–18 for each group) were compared and the distribution of the measured data showed a non-normal distribution. For the test, analytical data (absolute concentrations) was ranked from 1 (smallest) to  $N$  (largest). These ranks,  $R_{ij}$ , were then used for computation. Within each group, the average group rank,  $\bar{R}_j$ , was computed by the following equation:

$$\bar{R}_j = \frac{\left[ \sum_{i=1}^{n_j} R_{ij} \right]}{n_j} \quad (1)$$

**Table 2** Analytical methods and their detection limits used in this study

	Detection limit ( $\mu\text{g/l}$ )	Analytical method
Trace metals		ICP-MS
As	0.06	
Cd	0.02	
Cr	0.05	
Cu, Fe, Pb	0.03	
Mn	0.1	
Zn	0.6	
Detected volatile organic compounds (VOCs)		GC-MSD
Toluene, tert-butylbenzene, chloroform, carbon tetrachloride, bromodichloromethane, 1,1,1-trichloroethane (1,1,1-TCA), 1,2-dichloroethane (1,2-DCA), 1,1,2-trifluoro-1,2,2-trichloroethane (CFC113)	0.1	
Trichloroethene (TCE), 1,1-dichloroethene (1,1-DCE), methylene chloride, bromoform, 1,1-dichloroethane (1,1-DCA), 1,2-dichloropropane, 1,1,2-trichloroethane (1,1,2-TCA)	0.2	
MTBE, cis-1,2-dichloroethene (c-DCE), tetrachloroethene (PCE), dibromochloromethane	0.5	

The  $\bar{R}_j$  was then compared to the overall average rank,  $\bar{R} = (N + 1)/2$ , squaring and weighting by sample size, to form the test statistic  $K$ :

$$K = \frac{12}{N(N+1)} \times \sum_{j=1}^k n_j \left[ \bar{R}_j - \frac{N+1}{2} \right]^2. \quad (2)$$

The null hypothesis that the concentration of individual chemicals is not significantly different according to land use was tested using the Kruskal–Wallis (K–W) test; if the  $K$  value was larger than  $\chi^2_{1-\alpha, (k-1)}$ , the  $1-\alpha$  quantile of a chi-square distribution with  $(k-1)$  degrees of freedom, then the null hypothesis was rejected.

## Results and discussion

### Trace metals

Trace metals naturally occur in groundwater and their background concentrations are usually around at least

two orders of magnitude. Under certain land-use conditions, however, trace metals may occur in groundwater at higher concentrations. Table 3 summarizes the concentrations of trace metals (Fe, Mn, As, Cr, Pb, Zn, Cd, Cu) in relation to land use in Seoul. Comparison of the data with the US EPA's maximum contaminant levels (MCLs) and Korea Drinking Water Standards (KDWSs) showed that most of the considered metals did not exceed the regulation levels. However, some localities showed exceeding levels of Fe (two sites in the traffic areas and three sites in the industrial areas), Mn (two sites in the residential areas, one site in the traffic areas, and three sites in the industrial area), and Cu (one site in the traffic areas). The concentrations of most trace metals were remarkably low in the less-developed areas (Fig. 4). On the other hand, agricultural areas are characterized by high concentrations of Zn (average 229 µg/l); traffic areas by Cu (average 186 µg/l); and industrial areas by significant enrichments of most metals such as Fe (average 2,276 µg/l), Mn (average

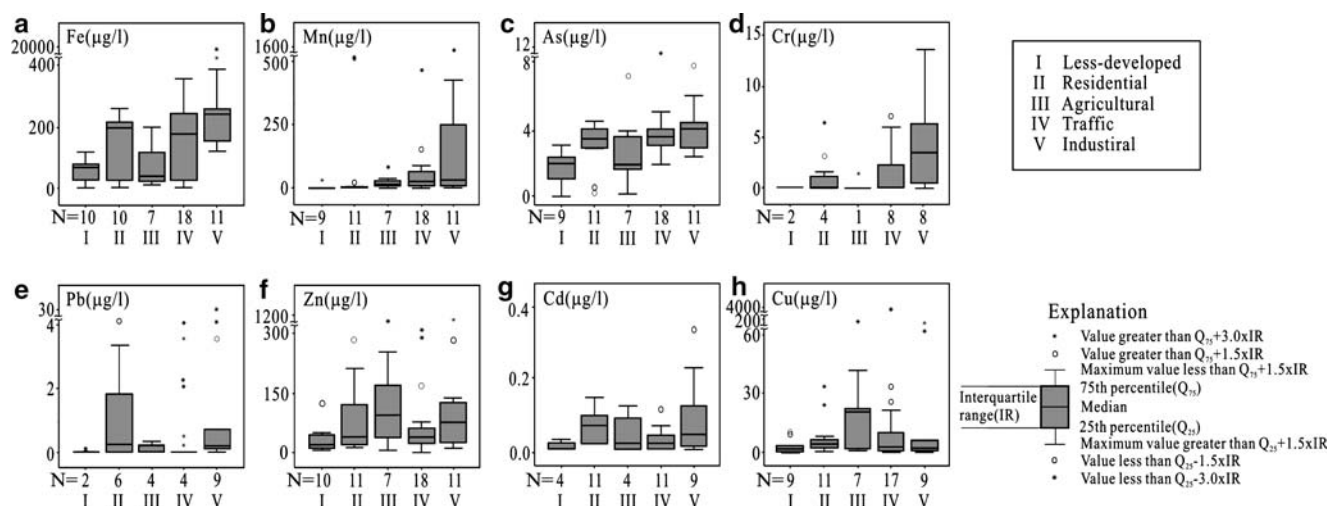
**Table 3** Basic statistics of the concentrations of trace metals in urban groundwater ( $N=57$ ), Seoul, Korea

Land use <sup>a</sup>	Concentration (µg/l)							
	Fe	Mn	As	Cr	Pb	Zn	Cd	Cu
Less-developed ( $N=10$ )								
Average	61.6	4.3	1.99	0.07	0.03	36.2	0.02	3.4
Median	70.2	0.8	2.14	0.03	0.02	22.8	0.02	2.2
Maximum	122.7	32.5	3.30	0.44	0.14	135.4	0.03	10.9
Minimum	1.9	<0.1	<0.06	<0.05	<0.03	7.2	<0.02	<0.03
Residential ( $N=11$ )								
Average	141.9	129.7	3.22	1.07	1.18	91.9	0.07	8.7
Median	190.4	5.8	3.61	0.03	0.28	45.0	0.07	4.8
Maximum	259.4	722.4	4.66	6.32	5.70	289.8	0.15	33.6
Minimum	<0.03	0.3	0.40	<0.05	<0.03	17.3	0.03	1.1
Agricultural ( $N=7$ )								
Average	83.2	20.3	2.92	0.31	0.17	229.5	0.05	37.7
Median	44.3	10.2	2.25	0.03	0.25	120.0	0.03	20.5
Maximum	197.5	77.2	7.10	2.00	0.40	935.1	0.12	160.1
Minimum	15.6	0.3	0.40	<0.05	<0.03	11.0	<0.02	2.4
Traffic ( $N=18$ )								
Average	161.9	51.7	4.07	1.29	0.53	78.6	0.04	186.1
Median	175.8	9.5	3.78	0.03	0.02	39.6	0.03	4.1
Maximum	354.8	467.6	10.7	6.09	5.00	392.7	0.11	3212.6
Minimum	6.9	0.1	2.25	<0.05	<0.03	2.7	<0.02	<0.03
Industrial ( $N=11$ )								
Average	2275.6	248.0	4.21	4.15	3.20	171.5	0.09	21.1
Median	242.2	41.5	4.08	3.44	0.33	86.1	0.05	2.6
Maximum	17450.8	1432.1	7.70	13.5	23.5	964.6	0.34	117.5
Minimum	134.3	0.4	2.63	<0.05	<0.03	14.2	<0.02	<0.03
Drinking water standards								
EPA <sup>b</sup>	300	50	50	100	15	5,000	5	1,300
Korea <sup>c</sup>	300	300	50	50	50	1,000	10	1,000

<sup>a</sup>Numbers in parentheses indicate the number of studied groundwater wells

<sup>b</sup>U.S. EPA's maximum contaminant levels (MCLs) for drinking water (U.S. EPA 2001)

<sup>c</sup>Korean Drinking Water Standard (MOE 2002)



**Fig. 4** Box plots of trace metal concentrations in urban groundwater, Seoul, Korea

248 µg/l), As (average 4.21 µg/l), Cr (average 4.15 µg/l), Pb (average 3.20 µg/l), and Cd (average 0.09 µg/l) (Fig. 4).

The Kolmogorov–Smirnov (K–S) test was performed on the distribution of trace metals to determine whether parametric or non-parametric tests might be successfully employed (Table 4). Because all the *P* values were smaller than the significance level of 0.05 (Table 4), the distribution of all the trace metals was interpreted as non-normal. Therefore, a non-parametric test was used to investigate the effect of land use on the distribution of trace metals. The K–W test was applied to the proposed null hypothesis (i.e., no significant change of the concentrations of individual chemicals according to land use). The results showed that *P* values of six metals (Fe, Mn, As, Cr, Pb, Cd) are smaller than the significance level of 0.05 (Table 5), which indicates that at the 95% confidence level, the distribution of those six metals in Seoul groundwater is significantly changed with the land use. Therefore, it is suggested that anthropogenic con-

tamination with respect to trace metals such as Fe, Mn, As, Cr, Pb and Cd has been proceeding in the industrial, traffic, and residential areas of Seoul.

#### Volatile organic compounds

Many kinds of VOCs may pose a potential risk to the environment because of their toxicity (e.g., pesticides and herbicides) and carcinogenicity (e.g., chloroform and TCE), and their potential adverse effects of reactions occurring within the natural system, such as oxygen consumption. As summarized in Appendix, a total of 69 compounds of VOCs were analyzed in this study. These are 47 species of chlorinated compounds (28 halogenated alkanes, 10 halogenated alkenes, 9 halogenated aromatics), 18 species of gasoline-related compounds (3 aromatic hydrocarbons, 14 alkyl benzenes, 1 ether) and 4 other species. Among 69 chemicals analyzed, 19 species were detected in Seoul groundwater. The basic statistics on the concentrations of detected 19 species are summarized in Table 6 according to the land use types in Seoul. More detailed data, together with detailed trace metal data, are available upon request to the corresponding author (S.-T. Yun).

As shown in Table 6 and Fig. 5, VOCs belonging to the chlorinated hydrocarbons were most frequently detected. A total of 16 chlorinated compounds were detected in a few localities, which include 12 species of halogenated alkanes [methylene chloride, chloroform, carbon tetrachloride, bromodichloromethane, dibromochloromethane, bromoform, 1,1-dichloroethane (1,1-DCA), 1,1,1-trichloroethane (1,1,1-TCA), 1,2-dichloroethane (1,2-DCA), 1,2-dichloropropane, 1,1,2-trichloroethane (1,1,2-TCA), 1,1,2-trichloro-1,2,2-trifluoroethane (CFC113)] and 4 species of halogenated alkenes [cis-1,2-dichloroethene

**Table 4** Results of the Kolmogorov–Smirnov (K–S) test for normality of the distribution of trace metals in urban groundwater (*N*=57), Seoul, Korea

Elements	K–S value	<i>P</i> value
Fe	0.491	0.000
Mn	0.366	0.000
As	0.155	0.002
Cr	0.326	0.000
Pb	0.383	0.000
Zn	0.279	0.000
Cd	0.258	0.000
Cu	0.456	0.000

**Table 5** Results of the Kruskal–Wallis test for the difference in distribution of groundwater trace metals according to land use, Seoul, Korea

Elements	Land use	Number of wells	Average rank	Chi-square	<i>P</i> value
Fe	Less-developed	10	17.00	16.673	0.002
	Residential	11	27.91		
	Agricultural	7	19.86		
	Traffic	18	30.67		
	Industrial	11	44.09		
Mn	Less-developed	10	14.20	11.296	0.023
	Residential	11	27.73		
	Agricultural	7	31.86		
	Traffic	18	32.11		
	Industrial	11	36.82		
As	Less-developed	10	12.35	15.983	0.003
	Residential	11	30.18		
	Agricultural	7	22.79		
	Traffic	18	35.42		
	Industrial	11	36.41		
Cr	Less-developed	10	21.20	12.883	0.012
	Residential	11	27.41		
	Agricultural	7	21.14		
	Traffic	18	29.72		
	Industrial	11	41.50		
Pb	Less-developed	10	20.00	13.358	0.010
	Residential	11	33.86		
	Agricultural	7	30.79		
	Traffic	18	23.47		
	Industrial	11	40.23		
Zn	Less-developed	10	17.55	8.602	0.072
	Residential	11	29.50		
	Agricultural	7	38.29		
	Traffic	18	27.67		
	Industrial	11	35.18		
Cd	Less-developed	10	16.00	12.149	0.016
	Residential	11	39.27		
	Agricultural	7	27.64		
	Traffic	18	27.19		
	Industrial	11	34.36		
Cu	Less-developed	10	20.75	7.681	0.104
	Residential	11	31.45		
	Agricultural	7	42.21		
	Traffic	18	29.17		
	Industrial	11	25.36		

(c-DCE), trichloroethene (TCE), tetrachloroethene (PCE), 1,1-dichloroethene (1,1-DCE)]. Among 18 analyzed species of gasoline-related compounds, only 2 species of alkyl benzenes (toluene, tert-butylbenzene) and 1 species of ethers [methyl tertiary butyl ether (MTBE)] were detected. On the other hand, halogenated aromatics and aromatic hydrocarbons were not detected at all. The kinds and concentrations of the VOCs detected in this study are similar with those reported for shallow urban groundwaters across the USA (Lopes and Bender 1998).

The detection frequency, as represented by the percentage of the samples with detection among 57 studied samples, was highest for toluene (86%), followed by chloroform (63%), methylene chloride (58%), TCE (40%), bromodichloromethane (32%), PCE and 1,1,1-TCA (each 25%), 1,1-DCA (18%), c-DCE (16%), MTBE (13%), tert-butylbenzene

(12%), carbon tetrachloride (9%), and others (each < 7%) (Fig. 5). These species were also documented as frequently encountered VOCs in shallow urban groundwaters (Lopes and Bender 1998). A comparison of data with the US EPA and Korean standards for drinking water (Table 6) showed that some compounds from a few localities exceeded the levels, such as TCE in six sampling sites (one site in the residential areas, one in the traffic areas, and four in the industrial areas), PCE in eight sites (one site in the residential areas, four in the traffic areas, and three in the industrial areas), 1,2-DCA in one site of the industrial areas, and 1,2-dichloropropane in one site of the industrial areas.

In relation to land use, more than one compound of VOCs was detected in all samples from the traffic, industrial, and residential areas. Table 7 shows the total numbers and kinds of VOCs detected in relation



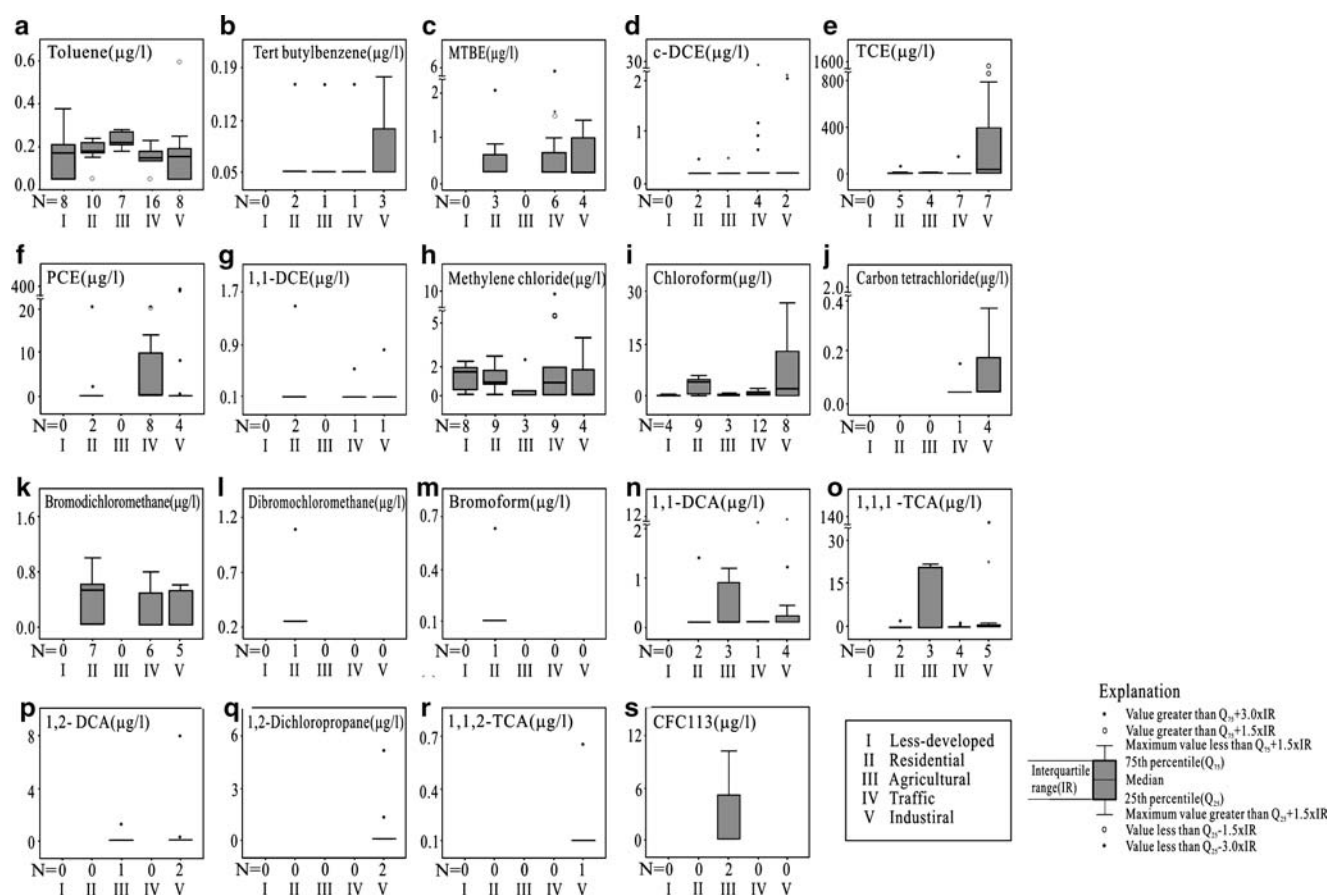
**Table 6** Basic statistics of the concentrations (unit: µg/l) of VOCs in urban groundwater (N=57), Seoul, Korea

Land use	Gasoline-related compounds				Chlorinated compounds																
	Alkyl benzenes		Ethers		Halogenated alkenes					Halogenated alkanes <sup>a</sup>											
	Toluene	Tert-butyl-benzene	MTBE		c-DCE	TCE	PCE	1,1-DCE	Meth. Chl	Chlfo	Carb. tetchl	Br-dichlmet	DiBrChl met	Brfo	1,1-DCA	1,1,1-TCA	1,2-DCA	1,2-Dichl Prop	1,1,2-TCA	CFC 113	
Less-developed (N=10)																					
Average	0.18	-	-	-	-	-	-	1.37	0.14	-	-	-	-	-	-	-	-	-	-	-	-
Median	0.17	-	-	-	-	-	-	1.70	0.05	-	-	-	-	-	-	-	-	-	-	-	-
Maximum	0.38	-	-	-	-	-	-	2.27	0.36	-	-	-	-	-	-	-	-	-	-	-	-
Minimum	<0.1	-	-	-	-	-	-	<0.2	<0.1	-	-	-	-	-	-	-	-	-	-	-	-
Residential(N=11)																					
Average	0.07	0.66	0.30	9.52	6.80	0.35	1.18	2.68	0.53	0.33	0.15	0.33	0.40	-	-	-	-	-	-	-	-
Median	0.18	0.25	0.25	0.10	0.25	0.10	0.80	4.20	0.53	0.25	0.10	0.10	0.05	-	-	-	-	-	-	-	-
Maximum	0.24	2.19	0.54	87.3	69.6	1.48	2.71	6.07	1.37	1.09	0.61	1.39	1.97	-	-	-	-	-	-	-	-
Minimum	<0.1	<0.5	<0.5	<0.2	<0.5	<0.5	<0.2	<0.1	<0.1	<0.5	<0.2	<0.2	<0.1	-	-	-	-	-	-	-	-
Agricultural(N=7)																					
Average	0.23	-	0.29	4.51	-	-	0.53	0.20	-	-	-	0.46	8.95	0.22	-	-	-	-	-	-	2.97
Median	0.05	-	0.25	1.80	-	-	0.10	0.05	-	-	-	0.10	0.05	0.05	-	-	-	-	-	-	0.05
Maximum	0.28	-	0.56	11.5	-	-	2.48	0.50	-	-	-	1.04	21.5	1.25	-	-	-	-	-	-	10.3
Minimum	0.18	<0.1	<0.5	<0.2	<0.5	<0.2	<0.2	<0.1	-	-	-	<0.2	<0.1	<0.1	-	-	-	-	-	-	<0.1
Traffic(N=18)																					
Average	0.15	0.78	1.48	13.3	5.99	0.12	2.02	1.26	0.06	0.23	-	-	0.49	0.11	-	-	-	-	-	-	-
Median	0.15	0.25	0.25	0.10	0.25	0.10	0.80	0.60	0.05	0.05	-	-	0.10	0.05	-	-	-	-	-	-	-
Maximum	0.23	5.47	20.3	223.8	35.4	0.52	9.25	4.98	0.16	0.79	-	-	7.04	0.95	-	-	-	-	-	-	-
Minimum	<0.1	<0.5	<0.5	<0.2	<0.5	<0.2	<0.2	<0.1	<0.1	<0.1	-	-	<0.2	<0.1	-	-	-	-	-	-	-
Industrial(N=11)																					
Average	0.18	0.56	1.54	309.1	63.4	0.17	1.09	7.9	0.26	0.25	-	-	1.18	12.6	0.80	0.67	0.15	-	-	-	-
Median	0.16	0.25	0.25	1.71	0.25	0.10	0.10	2.02	0.05	0.05	-	-	0.10	0.05	0.05	0.10	0.10	-	-	-	-
Maximum	0.60	1.34	10.01	1429.9	353.0	0.83	3.94	27.0	1.77	0.63	-	-	10.4	115.1	7.99	5.10	0.67	-	-	-	-
Minimum	<0.1	<0.5	<0.5	<0.2	<0.5	<0.2	<0.2	<0.1	<0.1	<0.1	-	-	<0.2	<0.1	<0.1	<0.2	<0.2	-	-	-	<0.2
Drinking water standard																					
EPA <sup>b</sup>	1,000	-	70	5	5	7	5	-	5	-	-	-	200	5	5	5	5	5	-	-	-
Korea <sup>c</sup>	700	-	-	30	10	30	20	80	2	-	-	-	100	-	-	-	-	-	-	-	-
Detection limit	0.1	0.5	0.5	0.2	0.5	0.2	0.2	0.1	0.1	0.1	0.5	0.2	0.1	0.1	0.1	0.2	0.2	0.1	0.2	0.2	0.1

<sup>a</sup>Br-dichl met Bromodichloro-methane; Brfo bromoform; Carb. tetchl carbon tetrachloride; Chlfo chloroform; DiBrChl met Dibromochloro-methane; Met. chl methylene chloride; 1,2-dichl prop 1,2-dichloro-propane

<sup>b</sup>U.S. EPA's maximum contaminant level (MCL) for drinking water (U.S. EPA 2001)

<sup>c</sup>Korean Drinking Water Standard (MOE 2002)



**Fig. 5** Box plots of VOCs concentrations in urban groundwater, Seoul, Korea

to land use. The detection frequency was obviously minimal in the less-developed areas (i.e., totaling 19 species in 10 samples, corresponding to a detection probability of circa 3% [= 19 species/(10 samples×69 species/sample)×100%], while groundwaters in the

industrial areas showed the most frequent detection (circa 9%). The summation of the concentrations of detected VOCs also showed that the industrial areas have the highest concentrations (average 25 µg/l) with a wide range [not detected (<0.1) to 1,429.9 µg/l]. In the less-developed areas only three compounds (i.e., methylene chloride, toluene, chloroform) were detected with very low concentrations; the summation of the 3

**Table 7** Total numbers of the detection of VOCs in groundwaters (N=57) from each land-use category, Seoul, Korea

Land use	Detected chemicals	Total numbers of detection <sup>a</sup>
Less-developed (N=10)	Dichloromethane, chloroform, toluene	19 (3%)
Residential (N=11)	Dichloromethane, chloroform, bromodichloromethane, dibromochloromethane, bromoform, 1,1-DCA, 1,1,1-TCA, c-DCE, TCE, PCE, 1,1-DCE, toluene, tert butylbenzene, MTBE	55 (7%)
Agricultural (N=7)	Dichloromethane, chloroform, 1,1-DCA, 1,1,1-TCA, 1,2-DCA, CFC113, c-DCE, TCE, toluene, tert butylbenzene	28 (6%)
Traffic (N=18)	Dichloromethane, chloroform, tetrachloromethane, bromodichloromethane, 1,1-DCA, 1, 1, 1-TCA, c-DCE, TCE, PCE, 1,1-DCE, toluene, tert butylbenzene, MTBE	76 (6%)
Industrial (N=11)	Dichloromethane, chloroform, tetrachloromethane, bromodichloromethane, 1,1-DCA, 1,1,1-TCA, 1,2-DCA, 1,2-Dichloropropane, 1,1,2-TCA, c-DCE, TCE, PCE, 1,1-DCE, toluene, tert butylbenzene, MTBE	65 (9%)

<sup>a</sup> Numbers in parentheses indicate the probability of VOCs detection, calculated using an equation: probability (%) = [(total number of detection)/(number of sample×69 species/sample)×100%

**Table 8** Results of the Kolmogorov–Smirnov test for the normality of the distribution of VOCs in groundwater ( $N = 57$ ), Seoul, Korea

	Kolmogorov–Smirnov value	<i>P</i> value
Toluene	0.151	0.002
Tert-butylbenzene	0.522	0.000
MTBE	0.418	0.000
c-DCE	0.441	0.000
TCE	0.479	0.000
PCE	0.424	0.000
1,1-DCE	0.528	0.000
Methylene chloride	0.243	0.000
Chloroform	0.323	0.000
Carbon tetrachloride	0.485	0.000
Bromodichloromethane	0.403	0.000
Dibromochloromethane	0.535	0.000
Bromoform	0.535	0.000
1,1-DCA	0.430	0.000
1,1,1-TCA	0.454	0.000
1,2-DCA	0.509	0.000
1,2-Dichloropropane	0.529	0.000
1,1,2-TCA	0.535	0.000
CFC113	0.540	0.000

species was not detected ( $<0.1$ ) to  $2.3 \mu\text{g/l}$  (average  $0.6 \mu\text{g/l}$ ) (Table 6). This suggests that urban groundwater contamination by VOCs appears to be significantly low in the less-developed areas, compared to areas of other land uses.

The present study shows that anthropogenic contamination especially by TCE and PCE is significant in urban groundwater. The very high concentration of TCE was observed in the industrial areas (average  $309.1 \mu\text{g/l}$ ), followed by the traffic (average  $13.3 \mu\text{g/l}$ ), residential (average  $9.5 \mu\text{g/l}$ ), agricultural (average  $4.5 \mu\text{g/l}$ ), and less-developed (not detected,  $<0.2 \mu\text{g/l}$ ) areas. Likewise, the average concentration of PCE was significantly higher in the industrial areas ( $63.4 \mu\text{g/l}$ ) than the residential ( $6.8 \mu\text{g/l}$ ), traffic ( $6.0 \mu\text{g/l}$ ), and less-developed and agricultural areas (not detected,  $<0.5 \mu\text{g/l}$ ) (Table 6; Fig. 5). The measured concentrations of TCE and PCE frequently exceeded the US EPAs and Korean Drinking Water Standards in many of the industrialized and traffic areas. This indicates that TCE and PCE may cause serious impacts on ecosystems and human health and should therefore be carefully monitored in Seoul.

A non-parametric statistical test was conducted to confirm the dependence of VOCs contamination upon land use. The K–S test showed that all the *P* values for detected VOCs were smaller than the significance level of 0.05 (Table 8), suggesting that the distribution of detected species can be considered to be non-normal. Sequentially, the K–W test was performed as a non-parametric statistical analysis to compare the distribution of VOCs among different land-use types.

The results showed that for seven compounds (toluene, TCE, PCE, chloroform, carbon tetrachloride, bromodichloromethane, CFC113) among 19 detected species, the *P* values are smaller than the significance level (0.05) (Table 9). This may indicate that the occurrence of these compounds closely depends upon the land use. Accordingly, those seven compounds may reflect the progress of anthropogenic contamination and can be effectively used as indicators to identify the degree of anthropogenic contamination in relation to land use. In comparison, six trace metals (Fe, Mn, As, Cr, Pb, Cd) with the *P* values of  $<0.05$  (Table 5) can also be recommended as indicators of anthropogenic contamination in Seoul groundwater. Furthermore, three compounds (TCE, PCE, chloroform) among the seven species are likely the best parameters in evaluating the effect of land use on groundwater quality in Seoul because they occur frequently and show relatively high concentrations.

## Summary and conclusions

The present study was performed to investigate the contamination of Seoul groundwater by trace metals and VOCs, focusing on the relationship between anthropogenic contamination and land use. The land use was classified into five categories: less-developed, residential, agricultural, traffic, and industrial. For research purposes, a total of 57 groundwater samples were collected from preexisting wells in use (average 94 m deep) and they were analyzed for eight trace metals (Fe, Mn, As, Cr, Pb, Zn, Cd, Cu) by ICP-MS and 69 VOCs by GC-MSD. Among the 69 compounds of VOCs, only 19 species were detected. The water quality data were statistically analyzed using the K–W test (a non-parametric statistical tool) to understand land-use control on groundwater contamination.

This study verified that the concentrations and spatial distribution of some trace metals (especially, Fe, Mn, As, Cr, Pb, Cd) and VOCs (especially, TCE, PCE and chloroform; and potentially toluene, carbon tetrachloride, bromodichloromethane, and CFC113) are significantly influenced by the land use in Seoul. The groundwaters in the less-developed areas are the least contaminated, as reflected by very low concentrations (if detected) of trace metals and VOCs. On the contrary, groundwaters in the industrial areas are significantly contaminated by some trace metals and VOCs. Though the current concentration levels for the examined trace metals and VOCs, for the most part, do not exceed the drinking water standards suggested by US EPA and Korea Ministry of Environment, PCE (eight sites), TCE (six sites), Mn (six sites), Fe (five sites), Cu (one site), 1,2-DCA (one site),

**Table 9** Results of the Kruskal–Wallis test for the difference in distribution of groundwater VOCs according to land use, Seoul, Korea

VOC	Land use <sup>a</sup>	Average rank	Chi-square	<i>P</i> value
Toluene	Less-developed (10)	27.70	10.474	0.033
	Residential (11)	32.50		
	Agricultural (7)	45.71		
	Traffic (18)	23.08		
	Industrial (11)	25.73		
Tert-butylbenzene	Less-developed (10)	25.50	4.912	0.296
	Residential (11)	30.59		
	Agricultural (7)	29.50		
	Traffic (18)	27.06		
	Industrial (11)	33.45		
MTBE	Less-developed (10)	22.50	7.011	0.135
	Residential (11)	30.64		
	Agricultural (7)	22.50		
	Traffic (18)	32.11		
	Industrial (11)	32.32		
c-DCE	Less-developed (10)	24.50	2.670	0.614
	Residential (11)	29.05		
	Agricultural (7)	28.29		
	Traffic (18)	31.06		
	Industrial (11)	30.14		
TCE	Less-developed (10)	17.50	10.978	0.027
	Residential (11)	29.91		
	Agricultural (7)	34.64		
	Traffic (18)	27.47		
	Industrial (11)	37.45		
PCE	Less-developed (10)	22.00	9.987	0.041
	Residential (11)	27.09		
	Agricultural (7)	22.00		
	Traffic (18)	34.50		
	Industrial (11)	32.73		
1,1,-DCE	Less-developed (10)	27.00	3.706	0.447
	Residential (11)	32.36		
	Agricultural (7)	27.00		
	Traffic (18)	28.50		
	Industrial (11)	29.55		
Methylene chloride	Less-developed (10)	34.10	3.942	0.414
	Residential (11)	32.55		
	Agricultural (7)	21.57		
	Traffic (18)	29.58		
	Industrial (11)	24.59		
Chloroform	Less-developed (10)	16.00	15.524	0.004
	Residential (11)	38.36		
	Agricultural (7)	17.57		
	Traffic (18)	30.89		
	Industrial (11)	35.64		
Carbon tetrachloride	Less-developed (10)	26.50	13.659	0.008
	Residential (11)	26.50		
	Agricultural (7)	26.50		
	Traffic (18)	27.97		
	Industrial (11)	37.05		
Bromodichloro-methane	Less-developed (10)	20.00	14.902	0.005
	Residential (11)	39.82		
	Agricultural (7)	20.00		
	Traffic (18)	28.83		
	Industrial (11)	32.36		
Dibromochloro-methane	Less-developed (10)	28.50	4.182	0.382
	Residential (11)	31.09		
	Agricultural (7)	28.50		
	Traffic (18)	28.50		
	Industrial (11)	28.50		

**Table 9** (Contd.)

VOC	Land use <sup>a</sup>	Average rank	Chi-square	P value
Bromoform	Less-developed (10)	28.50	4.182	0.382
	Residential (11)	31.09		
	Agricultural (7)	28.50		
	Traffic (18)	28.50		
	Industrial (11)	28.50		
1,1-DCA	Less-developed (10)	24.00	8.488	0.075
	Residential (11)	29.55		
	Agricultural (7)	35.57		
	Traffic (18)	25.78		
	Industrial (11)	34.09		
1,1,1-TCA	Less-developed (10)	22.00	8.557	0.073
	Residential (11)	27.36		
	Agricultural (7)	36.00		
	Traffic (18)	27.33		
	Industrial (11)	35.27		
1,2-DCA	Less-developed (10)	27.50	6.863	0.143
	Residential (11)	27.50		
	Agricultural (7)	31.57		
	Traffic (18)	27.50		
	Industrial (11)	32.68		
1,2-Dichloro-propane	Less-developed (10)	28.00	8.513	0.074
	Residential (11)	28.00		
	Agricultural (7)	28.00		
	Traffic (18)	28.00		
	Industrial (11)	33.18		
1,1,2-TCA	Less-developed (10)	28.50	4.182	0.382
	Residential (11)	28.50		
	Agricultural (7)	28.50		
	Traffic (18)	28.50		
	Industrial (11)	31.09		
CFC113	Less-developed (10)	28.00	14.545	0.006
	Residential (11)	28.00		
	Agricultural (7)	36.14		
	Traffic (18)	28.00		
	Industrial (11)	28.00		

<sup>a</sup>Numbers in parentheses indicate the number of studied groundwater wells

and 1,2-dichloropropane (one site) showed the local contamination to an undrinkable level. In particular, groundwaters in the industrial areas have significantly higher concentrations of most of the trace metals and detected VOCs. The contamination by TCE and PCE is noticeable and locally serious in the industrial and traffic areas and therefore should be carefully monitored with special attention.

The results of this study show that land use is an important factor in urban groundwater quality. In particular, the concentrations of some trace metals (Fe, Mn, As, Cr, Pb, Cd) and VOCs (TCE, PCE, chloroform) are significantly controlled by land use. Those chemicals can therefore be used as reliable indicators on the progress of anthropogenic contami-

nation in relation to land use. This study also suggests that careful and regular monitoring of groundwater for trace metals and VOCs is required in Seoul to safeguard the public water supply. In addition, monitoring works should be carefully designed to reflect the change in land-use patterns.

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## Appendix

Summary of the 68 compounds of VOCs analyzed in this study

Compound (IUPAC nomenclature)	Common name (alternative name)	Major industrial use	Detection ( <i>N</i> = 19) in this study <sup>a</sup>
<b>1. Chlorinated compounds</b>			
<i>Halogenated alkanes</i>			
Chloromethane	Methyl chloride		
Dichloromethane	Methylene chloride	Solvent	Y
Trichloromethane	Chloroform	Solvent	Y
Tetrachloromethane	Carbon tetrachloride		Y
Bromomethane	Methyl bromide		
Dibromomethane			
Tribromomethane	Bromoform	Solvent	Y
Dibromochloromethane		Solvent	Y
Bromochloromethane			
Bromodichloromethane		Organic synthesis	Y
Chloroethane	Ethyl chloride		
1,1-Dichloroethane	Ethylidenedichloride		Y
1,2-Dichloroethane	Ethylenedichloride	Solvent	Y
1,1,1-Trichloroethane	Methyl chloroform	Solvent	Y
1,1,2-Trichloroethane		Solvent	Y
1,1,1,2-Tetrachloroethane			
1,1,2,2-Tetrachloroethane			
Pentachloroethane			
Hexachloroethane			
1,2-Dibromoethane	EDB		
1,1-Dichloropropane			
1,2-Dichloropropane			Y
2,2-Dichloropropane			
1,3-Dichloropropane			
1,2,3-Trichloropropane		Fumigant	
1,2-Dibromo-3-chloropropane	DBCP		
Trichlorofluoromethane	Freon 11, CFC11		
1,1,2-Trichloro-1,2,2-trifluoroethane	Freon113, CFC113		Y
<i>Halogenated alkenes</i>			
Chloroethane	Vinyl chloride		
1,1-Dichloroethene			Y
<i>cis</i> -1,2-Dichloroethene		Solvent	Y
<i>trans</i> -1,2-Dichloroethene			
Trichloroethene	TCE	Solvent	Y
Tetrachloroethene	Perchloroethylene, PCE	Solvent	Y
1,1-Dichloropropene			
<i>cis</i> -1,3-Dichloropropene			
<i>Trans</i> -1,3-dichloropropene			
Hexachlorobutadiene			
<i>Halogenated aromatics</i>			
Chlorobenzene			
1,2-Dichlorobenzene	<i>o</i> -Dichlorobenzene		
1,3-Dichlorobenzene	<i>m</i> -Dichlorobenzene	Solvent	
1,4-Dichlorobenzene	<i>p</i> -Dichlorobenzene	Fumigant	
1,2,3-Trichlorobenzene		Organic synthesis	
1,2,4-Trichlorobenzene			
Bromobenzene			
2-Chlorotoluene			
4-Chlorotoluene			
<b>2. Gasoline-related compounds</b>			
<i>Aromatic hydrocarbons</i>			
Benzene		Gasoline	
Styrene	Vinyl benzene	Organic synthesis	
Naphthalene		Gasoline	

## Appendix (Contd.)

Compound (IUPAC nomenclature)	Common name (alternative name)	Major industrial use	Detection ( <i>N</i> = 19) in this study <sup>a</sup>
<i>Alkyl benzenes</i>			
Methylbenzene	Toluene	Gasoline	Y
Ethylbenzene		Gasoline	
<i>n</i> -Propylbenzene			
<i>iso</i> -Propylbenzene	Cumene	Organic synthesis	
1-Methyl-4-(2-methyl ethyl) benzene	<i>p</i> -Isopropyl toluene		
<i>n</i> -Butylbenzene		Gasoline	
1,2-Dimethylbenzene	<i>o</i> -Xylene	Gasoline	
1,3-dimethylbenzene	<i>m</i> -Xylene	Gasoline	
1,4-Dimethylbenzene	<i>p</i> -Xylene	Gasoline	
1,2,4-Trimethylbenzene			
1,3,5-Trimethylbenzene			
<i>sec</i> -Butylbenzene			
<i>tert</i> -Butylbenzene			Y
4-Isopropyltoluene			
<i>Ethers</i>			
Methyl tertiary-butyl ether	MTBE	Oxygenate	Y
<b>3. Others</b>			
2-Propenenitrile	Acrylonitrile		
<i>n</i> -Hexane			
Methylethyl ketone			
Bis(2-chloroisopropyl) ether			

<sup>a</sup>Detected species in urban groundwater, Seoul (this study)

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